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CONCORDE AIR SAMPLING PROGRAM. INTERCALIBRATIONS AND COLLABORAT--ETC(U)

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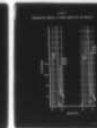
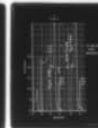
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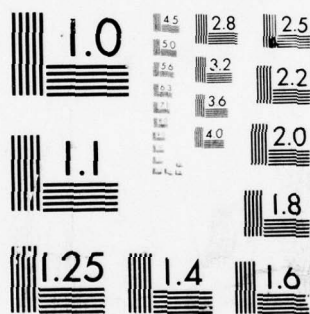
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# CONCORDE AIR SAMPLING PROGRAM

## INTERCALIBRATIONS AND COLLABORATIVE MEASUREMENTS

By  
**R. A. Rasmussen**



**FINAL REPORT**  
**September 1978**

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16. Abstract Joint analyses of air samples similar to the operational type of samples obtained on Concorde flights were accomplished at A.E.R.E. Harwell in July 1978 between the Oregon Graduate Center and the Division of Environmental and Medical Sciences, Harwell. The studies were preliminary to directly comparing the data previously obtained by the contractor on the same species during an extensive series of high altitude flights made in 1975-1977. The interlaboratory calibrations and comparisons were successful. A second round of sample exchanges are in progress. Separately the joint studies measured for the first time the concentration of $CF_4$ in the ambient atmosphere as well as the related trace gases $COS$ and $CS_2$ in several samples of volcanic emissions. The report includes a discussion of the Concorde program as to air sampling capabilities, operation, sampling schedule and the uniqueness of related opportunities of the Concorde Air Sampling Program.		
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## I. INTRODUCTION

The immediate objective of this study was to conduct joint analyses between the Oregon Graduate Center and the Division of Environmental and Medical Sciences, Harwell, of air samples similar to the operational type of samples obtained on Concorde flights. The longer term objective is to compare the data obtained on the Concorde Air Sampling Program with the data previously obtained by OGC on the same species during an extensive high altitude sampling program conducted from 1975 to 1977. The studies are preliminary to better understanding the role and distribution of trace gases in the upper atmosphere and the related effects of aviation on the stratosphere. The study involved intercalibration, joint analysis of a variety of air samples and a review of the air sampling capabilities of the Concorde program.

## II. SUMMARY

The Concorde air sampling program is a viable program that offers unique advantages of obtaining repetitive data on the seasonal and altitudinal variation in the concentration distribution of the trace gases in the lower stratosphere over the route between Dulles (Washington, DC) and Heathrow (London, UK).

State-of-the-art measurement methods employing both ec-gc and gc-ms are used at Harwell to measure seven trace gases ( $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{COS}$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ). The results for the first 16 out of 20 flights are very encouraging and indicate that a new understanding of the altitudinal, longitudinal and seasonal variation of the composition of the upper atmosphere will be deduced from the data obtained. Continued operation of the program for an additional 30 flights is almost certain to provide the needed data to better understand the distribution and budgets of the upper atmosphere's trace gases.

The program would be considerably strengthened by a provision for the exchange of samples with other laboratories for corroborating analyses and/or additional measurements of species not measured by Harwell. The species recommended for further study are  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CHCl}_3$ ,  $\text{SF}_6$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{HCl}_3$ , and  $\text{C}_2\text{Cl}_4$ . These species were originally listed to be analyzed in the Concorde sampling program. Because of significant interlaboratory (Harwell vs. OGC) differences in the concentrations for the fluorocarbons 11 and 12 and carbon tetrachloride a continuing effort for further intercomparison studies is needed. In this way, the Concorde data can be more directly compared to related lower stratospheric-upper tropospheric data obtained on high altitude Lear-jet flights made in 1975, 1976 and 1977.

The atmospheric concentration of carbon tetrafluoride ( $\text{CF}_4$ ) was measured for the first time in a variety of ambient air samples. The data obtained on 11 different samples suggested a mean global concentration of  $64 \pm 13$  pptv. Within the precision of analyses no interhemispheric difference was indicated. The importance of  $\text{CF}_4$  to upper atmospheric processes is unknown. In companion gc-ms analyses COS and  $\text{CS}_2$  were measured in several samples of volcanic emissions. The concentrations observed ranged from 20 to 100 ppbv. Their presence in volcanic emissions is relevant to the ubiquitously observed concentration of COS at  $\sim 500$  ppt in upper tropospheric and lower tropospheric air samples. The sulfate aerosols characteristic of the Junge layer at 18 to 20 km are possibly derived from the sulfur that reaches the lower stratosphere via COS. Separate publication of these new results is intended.



### III. RESULTS

#### A. Trace Gas Analyses

##### 1. Analysis of Concorde Air Samples

No Concorde air samples were available for study during my work period at Harwell. Accordingly the trace gases in air samples contained in similar types of stainless steel bottles brought from OGC to Harwell were analyzed. The samples studied were representative of the global atmosphere: South Pole Antarctica, Godley Head, on the south island, New Zealand and northern hemisphere oceanic air samples collected at Cape Meares, Oregon. In addition three samples of volcanic emissions from Hawaii were provided for analyses.

The compressed air in the bottles was studied with the same methods and instrumentation used at Harwell for analyzing the Concorde air samples. In this way the analyses served as an intercomparison of measurement approach and capability between OGC and Harwell. The  $N_2O$ , F-12, F-11 and  $CCl_4$  species were measured jointly by Drs. Penkett and Sandalls' laboratories with electron capture gas chromatography. The  $COS$ ,  $CH_3Cl$  and  $CH_4$  analyses were performed by Drs. S. Penkett and N. Prosser on a V.G. Micromass-16 mass spectrometer equipped with a gas chromatograph. The above ec-gc study methods were used for the interlaboratory calibration of the fluorocarbons 11 and 12 and carbon tetrachloride by Dr. Sandalls. The  $N_2O$  measurements and related fluorocarbon 11 and carbon tetrachloride analyses were performed in Dr. Penkett's laboratory.

The results for the analysis of the Cape Meares sample #113 performed by Dr. Sandalls are given in Table I. The differences in the values are significant. Part of the reason for the difference may be in the values assigned to the absolute primary reference standards used for the respective calibrations



Table I

Halocarbon	Sandalls Measurement (pptv)	Rasmussen Measurement (pptv)
F-11	208 $\pm$ 17	172 $\pm$ 2
F-12	308 $\pm$ 25	283 $\pm$ 2
CCl <sub>4</sub>	116 $\pm$ 9	146 $\pm$ 3

in each laboratory. Accordingly, if the differences are systematic they can be adjusted through further exchange of calibration standards. However it is also possible that the lower CCl<sub>4</sub> level in sample #113 reflects a change due to wall adsorption. Therefore, until further studies have been made it is difficult to directly compare the fluorocarbon data obtained on the six Concorde flights made between June 18, 1971 to January 15, 1978 with the tropospheric values obtained by OGC during the same time period over the Atlantic Ocean and in the Pacific Northwest (Table II).

Table II

Organization	Date	Altitude	Place	F-12 ppt	F-11 pptv	CCl <sub>4</sub> pptv	N <sub>2</sub> O ppbv
Harwell	6/77 to 1/78	16500 ft.	Atlantic Ocean	300	304	173	283
OGC	7/77	18000 ft.	Atlantic Ocean	263	155	135	330
OGC	1/78	0	Pacific Ocean	275	166	142	330

It is interesting that the intercalibration of CCl<sub>4</sub> values between myself and Dr. Sandalls' lab at Harwell were lower than the OGC submitted values, yet the comparable Concorde CCl<sub>4</sub> data obtained by Dr. Sandalls are significantly higher than OGC CCl<sub>4</sub> data over the Atlantic. The inconsistencies in the data require further measurements before they can be satisfactorily resolved.

The agreement between laboratories for fluorocarbon-12 is very good. The difference in the interlaboratory comparison was a 9% higher value on test sample #113 obtained by Harwell than OGC. The comparable Concorde fluorocarbon-12 data are only 12% higher than OGC's averaged July and January data. This is interpreted to be consistent with the expected difference between laboratories due to the use of different primary calibration standards. However, the large difference in fluorocarbon-11 values between Concorde samples and OGC data for July and January 1977 is believed to be due to contamination of fluorocarbon-11 in the Concorde samples. The interlaboratory comparison difference between OGC and Harwell for test sample #113 was only 21% for F-11.

Further information on the degree of agreement between OGC and Harwell halocarbon measurements are given in Table III, from analyses made in Dr. Penkett's laboratory. Whereas the agreement for F-11 is excellent, the  $\text{CCl}_4$  value is definitely lower as analyzed at Harwell. The results strongly suggest a stability problem similar to that observed by Dr. Sandalls analyses of the trace levels of  $\text{CCl}_4$  in the cylinders used (Sample bottles #113

Table III

Halocarbon	Penkett Measurement pptv	Rasmussen Measurement pptv
Sample #171		
F-11	$171 \pm 1.6$	$171 \pm .1$
$\text{CCl}_4$	$105 \pm 1.8$	$145 \pm 3$
$\text{N}_2\text{O}^*$	$343 \pm 2\%$	$329 \pm 1$
Sample #113		
$\text{N}_2\text{O}^*$	$314 \pm 2\%$	$330 \pm 2$
Outside Air	$294 \pm 2\%$	

\*  $\text{N}_2\text{O}$  Concentration in ppbv

and 171). The  $N_2O$  data also show more divergence than anticipated. The two samples are to be returned to OGC for a post analyses in order to determine the respective concentrations of the species under study as a function of changes related to storage time.

The lower  $N_2O$  values reported for the Concorde flights (283 ppbv) than obtained by OGC in global atmospheric samples (330 ppbv) is consistent with the comparison of Harwell's value for outside air (294 ppbv) and OGC's samples #113 and #171 which were determined by OGC to be 330 ppbv shortly after filling. The 11 to 14% lower  $N_2O$  values obtained at Harwell for  $N_2O$  than by OGC for ambient air are consistent in these analyses. However, the 5% lower value obtained by Harwell or sample #113 and the 4% higher value for #171 than measured by OGC are not consistent. At the present time there is no explanation for the discrepancy.

## 2. Related Tropospheric Trace Gas Measurement

Secondary objectives of the laboratory studies on air samples at Harwell were to:

- a) Identify whether or not  $CF_4$  was present in the atmosphere.
- b) Determine the  $CF_4$  level in samples of volcanic emissions.
- c) Analyze several air samples representative of different parts of the globe for COS and  $CS_2$ .

## 3. $CF_4$ Studies

The presence of  $CF_4$  in the atmosphere at a concentration of approximately 0.1 to 1 ppb was suggested by Gassman (4) from his analyses of trace levels of  $CF_4$  in high purity Krypton samples. Gassman suggested that the  $CF_4$  was enriched from the atmosphere during the cryogenic preparation of the high purity Krypton. The gc-ms analyses made at Harwell were conducted to determine whether or not  $CF_4$  was detectable in the ambient atmosphere and if so at what concentrations.

The study method used a preconcentration step for enriching the  $\text{CF}_4$  before injecting it into the gc-ms. The cryogenic trapping technique used had been used previously at Harwell for  $\text{COS}$  and  $\text{CS}_2$  studies (5). Essentially ambient air was allowed to liquify in a glass U-tube immersed in liquid nitrogen ( $\text{LN}_2$ ). The ends of the U-tube were fitted with Rotaflor<sup>®</sup> stopcocks. After the U-tube was approximately 2/3 to 3/4 full the liquid air was blown off by helium. The helium was purified by an immediate pre-passage through 40 ft. of 1/8-inch OD stainless steel tubing immersed in  $\text{LN}_2$ . This freeze-out train was sufficient to remove any  $\text{CF}_4$  (B.P. -  $128^\circ\text{C}$ ) from the helium as determined by gc-ms analyses of enriched helium blanks looking for  $\text{CF}_4$ . When the liquid air was gone from the U-tube trap, the stopcocks were closed. Removed from  $\text{LN}_2$  and equilibrated at room temperature, the trap was under positive pressure from the helium blanket in the trap. Syringe samples were filled directly from the side arms of the traps for injection into the gas chromatographic column.

For quantification both Krypton<sup>84</sup> (B.P.,  $-158^\circ\text{C}$ ) and Xenon<sup>132</sup> (B.P.,  $-107^\circ\text{C}$ ) were measured directly in 5 ml air samples and in freeze-out cryogenic preparations. Based upon an essentially 100% enrichment of  $\text{Kr}^{84}$  and  $\text{Xe}^{132}$  [bracketing  $\text{CF}_4$ , ( $-128^\circ\text{C}$ )] the data were taken to indicate that  $\text{CF}_4$  was quantitatively enriched. Subsequent analyses measured only  $\text{Xe}^{132}$  with the  $\text{CF}_4$  for use as an internal standard.  $\text{Xe}^{132}$  concentration in the air is 23 ppb based upon its isotope abundance of ~27% of total a Xenon atmospheric concentration of 84 ppb. Accordingly its fix atmospheric concentration provided an excellent internal standard for determining enrichment ratios of the samples studied.

The gas chromatograph-mass spectrometer conditions of analyses were Hewlett-Packard 5700 series gas chromatograph with a 1/4" OD, 3 ft. glass column packed with 70-140 mesh Woelm Alumina GSC-120. Column temperature was held at



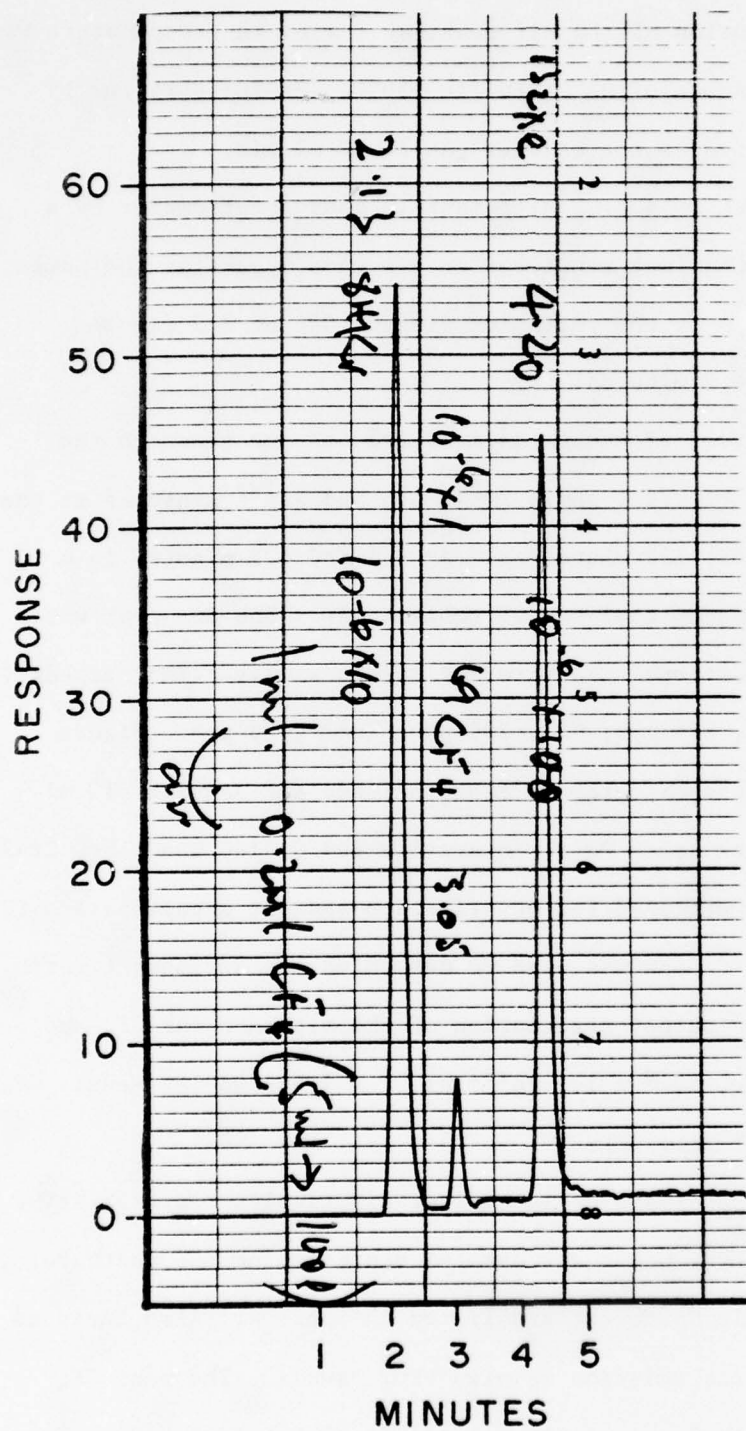
-20°C to enrich the 10 ml injections of the cryotrap contents onto the head of the column. After the elution of the air peak, at 2 min. the temperature was raised ballistically (in excess of 32°C/min) to +50°C. Helium purified by passage through LN<sub>2</sub> was used as the carrier gas at 40 ml/min.

The gc was interfaced to a V.G. Micromass-16 mass spectrometer by a jet separator. Mass 69 (CF<sub>3</sub>) was monitored as the major peak for the parent CF<sub>4</sub> species (minus F = CF<sub>3</sub>) at the retention time of CF<sub>4</sub> at 3.2 minutes. Xenon<sup>132</sup> was measured at 4.2 minutes.

Representative analyses of the gc-ms measurements are shown in the following three figures. Figure 1 shows Kr<sup>84</sup>, CF<sub>4</sub> and Xe<sup>132</sup> measured at their respective masses of 84, 69, 132 eluted at 2.2, 3.1 and 4.3 minutes in a subambient temperature program analyses of ambient air. The CF<sub>4</sub> peak was spiked by injection of additional CF<sub>4</sub> material to the sample. The respective concentrations are: Kr<sup>84</sup>, 570 ppb; CF<sub>4</sub>, 200 ppb; Xe<sup>132</sup>, 23 ppb. Figure 2 and 3 show CF<sub>4</sub> and Xe<sup>132</sup> chromatographed from enriched air samples (10 ml aliquots) representative of South Pole, Antarctica and Godley Head, New Zealand. The peak heights of each were used for quantitation against a calibration CF<sub>4</sub> standard in air. The Xe<sup>132</sup> peak was used to determine the enrichment ratio. The respective gain of the output attenuation of the recorder for CF<sub>4</sub> and Xe<sup>132</sup> are South Pole: CF<sub>4</sub>, 10<sup>-8</sup> x 10; Xe<sup>132</sup>, 10<sup>-5</sup> x 5 and Godley Head: CF<sub>4</sub>, 10<sup>-8</sup> x 10; Xe<sup>132</sup>, 10<sup>-6</sup> x 1 amps/volt.

The results from 21 analyses of 11 ambient air samples representative of Harwell environs and three other air samples representing the South Pole, New Zealand and the Pacific Northwest are listed in Table 4. Also included in the table are three volcanic emission samples from Hawaii. The mean CF<sub>4</sub> concentration for the 16 analyses of Harwell air is 63.6 ± 13.2 pptv. The mean of the other 3 air samples for 5 analyses is 64.4 ± 3.2 pptv. No

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FIGURE 1



$\text{Kr}^{84}$ ,  $\text{CF}_4$ ,  $\text{Xe}^{132}$

RESOLUTION CHECK



FIGURE 2

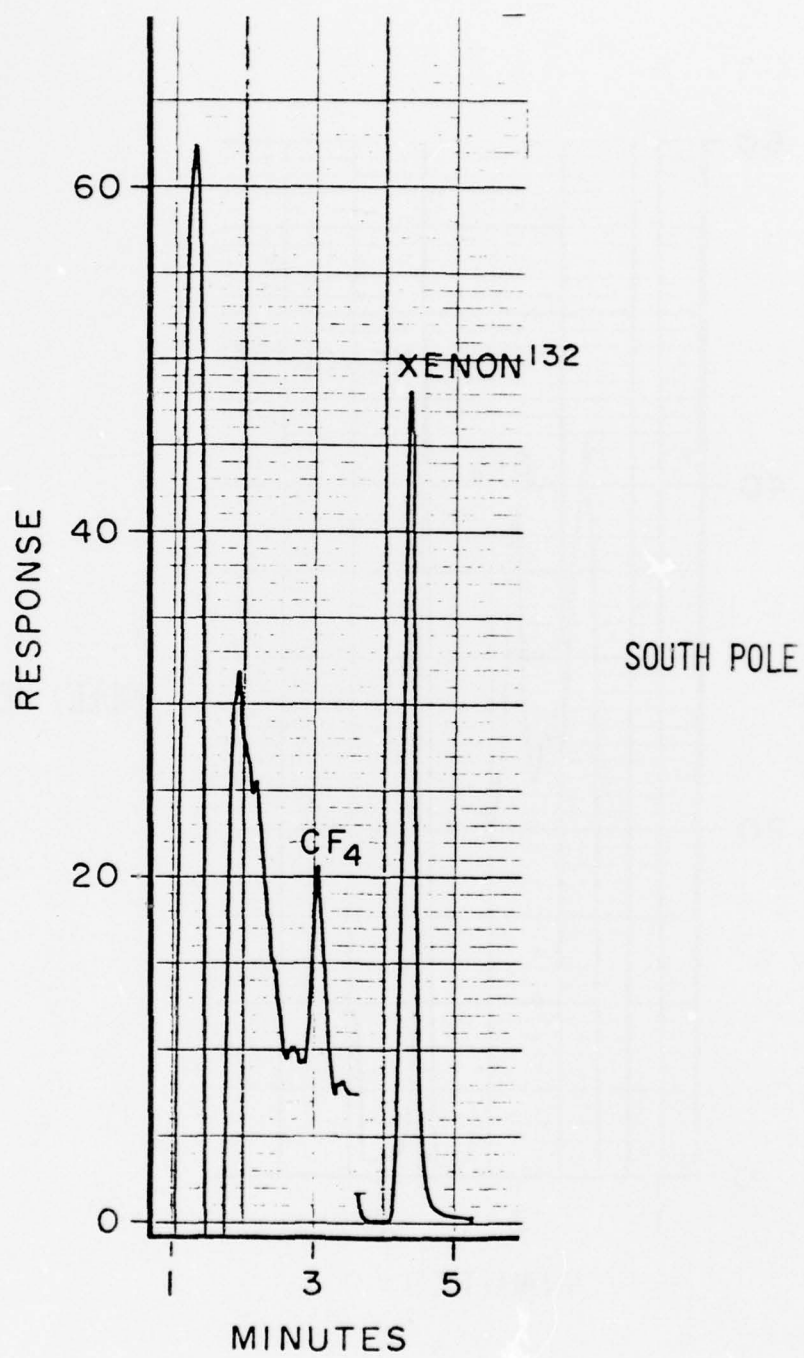
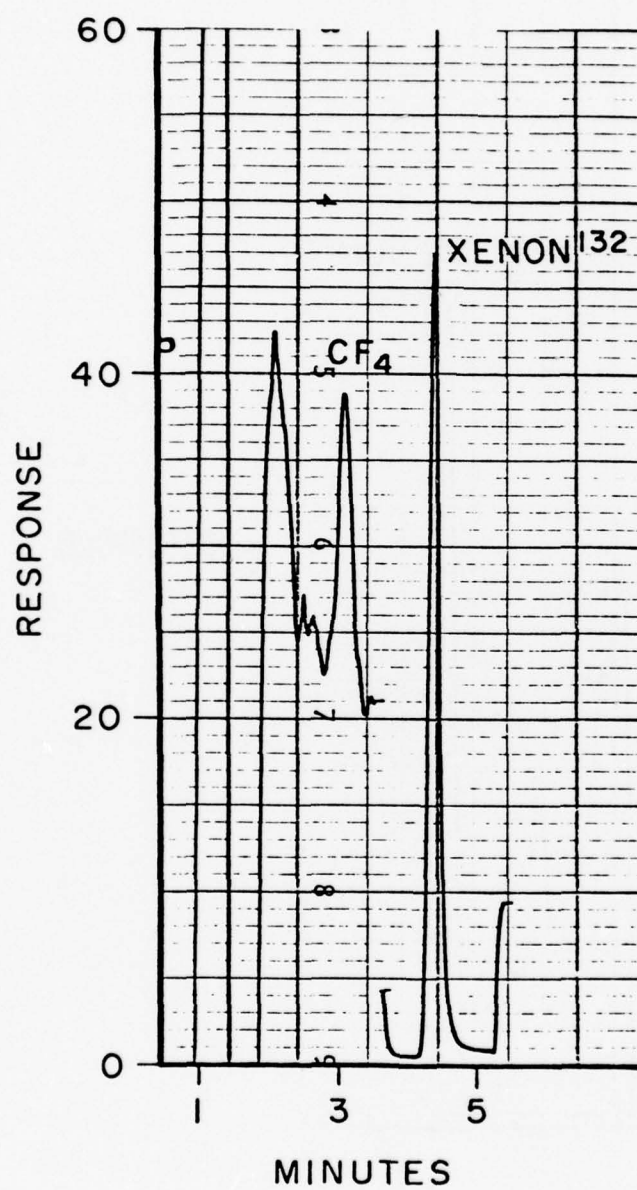


FIGURE 3



GODLEY HEAD

Table IV

CF<sub>4</sub> Measurement

Date of Analysis	Sample	Concentration Factor	CF <sub>4</sub> pptv
<u>HARWELL</u>			
17/7/78	OA	30.8	56.5
17/7/78	OA	16.1	66
		20.3 repeat	42
17/7/78	OA	15.9	58
		16.3 repeat	55
17/7/78	OA	19.5	59
18/7/78	OA	30.95	55
		34.52 repeat	43
18/7/78	OA	25.97	83
18/7/78	OA	29.41	71
		116.18 repeat	85
18/7/78	OA	10.3	74
19/7/78	OA	36.62	83
19/7/78	OA	6.02	69
		5.26 repeat	56
19/7/78	OA	30.16	62
<u>OTHER</u>			
19/7/78	PNW 171	8.20	63
		37.50 duplicate	67
20/7/78	S. Pole, Antarctica	15.04	64
	Antarctica	18.27 duplicate	60
	Godley Head, NZ	9.44	68
<u>VOLCANO</u>			
19/7/78	Iilewa, Hawaii	11.27	
		6.27 duplicate	48
20/7/78	MLC, Hawaii	12.39	46
		6.81 duplicate	51

OA = Outside Air

MLC = Mauna Loa Cauldera

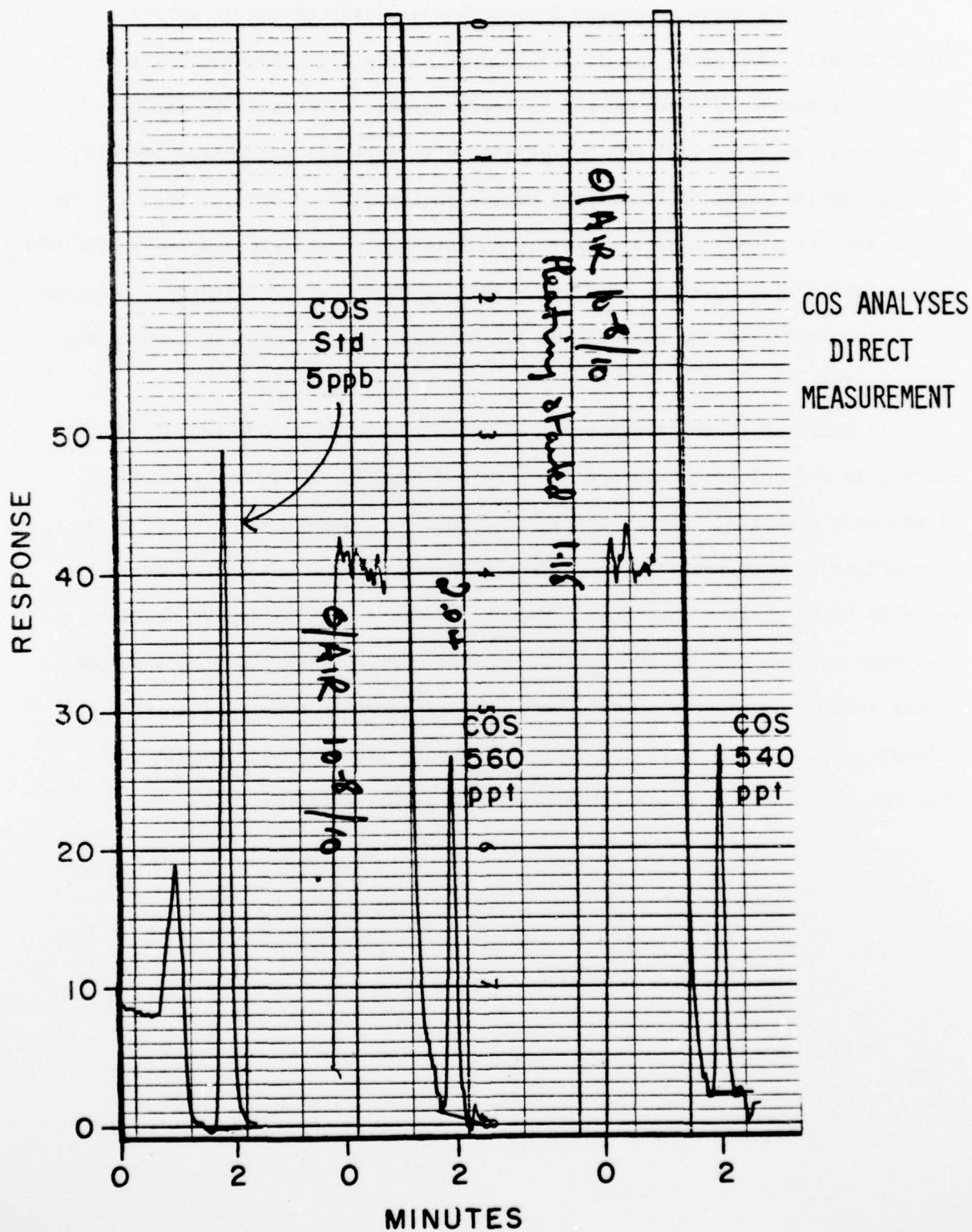
significant difference is shown although the variability in the Harwell values may be more than the variation in repetitive or duplicate analyses. Further work on the precision of analysis is needed before this can be accepted. Therefore at this time the data would suggest no interhemispheric difference.

Of possible equal interest is that the level of  $\text{CF}_4$  in the volcanic emissions representative of a hot fumerole in the cauldера of Mauna Loa (13000 ft.) and a much cooler vent on the northeast side of Kilauea at Iilewa show similar levels of  $\text{CF}_4$  but at significantly lower  $\text{CF}_4$  concentrations  $48.3 \pm 2.5$  ppt than ambient (64 pptv). Previously, Gassman (5) had suggested that volcanic emissions may be a source of  $\text{CF}_4$ . This may still be correct as the volcanic emissions studied are not representative of active magmatic gases released during a volcanic eruption. Also Mauna Loa's halide concentration is lower than volcanoes in general. The production of  $\text{CF}_4$  in electrolytic alumina reduction furnaces is known. However, the production of  $\text{CF}_4$  is not continuous but rather restricted to 5 to 10 minutes per day as the pot line goes through its periodic "Anode effect" (6). Further work in this area is continuing, to determine if anthropogenic sources could be responsible for the  $\text{CF}_4$  observed.

#### 4. COS and $\text{CS}_2$ Measurements

The conditions of analysis used to measure COS were similar to those used for  $\text{CF}_4$  except direct injection of 10 ml air samples onto the head of the column were used. This was possible because of the order of magnitude higher concentration of COS in ambient air (550 pptv). The column temperature was programmed from  $-10$  to  $+40^\circ\text{C}$ . The temperature program was begun at 1.2 minutes and COS eluted at 2 minutes. The chromatograms in Figure 4 show COS calibration sample of 5 ppbv at a gain of  $10^{-8} \times 2$  and a duplicate analysis of outside air showing 560 and 540 pptv respectively at gain of  $10^{-8} \times 10$  amps/volt.

FIGURE 4





The results shown in Figure 5 show that analyses of COS in ambient air at Harwell (550 pptv) and that in sample bottle #113 representative of the Pacific Northwest. The reason for the considerable difference is unknown since it was expected that COS concentration in northern hemisphere would be essentially the same. Further work on the variability of COS in clean air stored in the type of aluminum bottle used to collect compressed air samples by OGC and the stainless steel bottles used by Harwell in the Concorde flights is suggested.

The results of the analysis of the COS measurements made at Harwell are shown in Table 5.

In addition to the ambient air analyses the level of COS and CS<sub>2</sub> was studied in the volcanic emission samples from Hawaii. While low ppb levels of COS were expected, similar or higher levels of CS<sub>2</sub> were not. It is also appropriate to note that the presence of COS and CS<sub>2</sub> had not been previously verified to be present in volcanic emissions even though extensive studies have been made on H<sub>2</sub>S and SO<sub>2</sub> emissions. The three volcano samples show COS levels that do not vary as much as would be expected of such dissimilar volcanic samples. The range of 24 to 58 ppbv is not very much considering that the SO<sub>2</sub> levels in these three sites are widely different.



FIGURE 5

COMPARISON OF AMBIENT VS STORED SAMPLES FOR COS ANALYSES

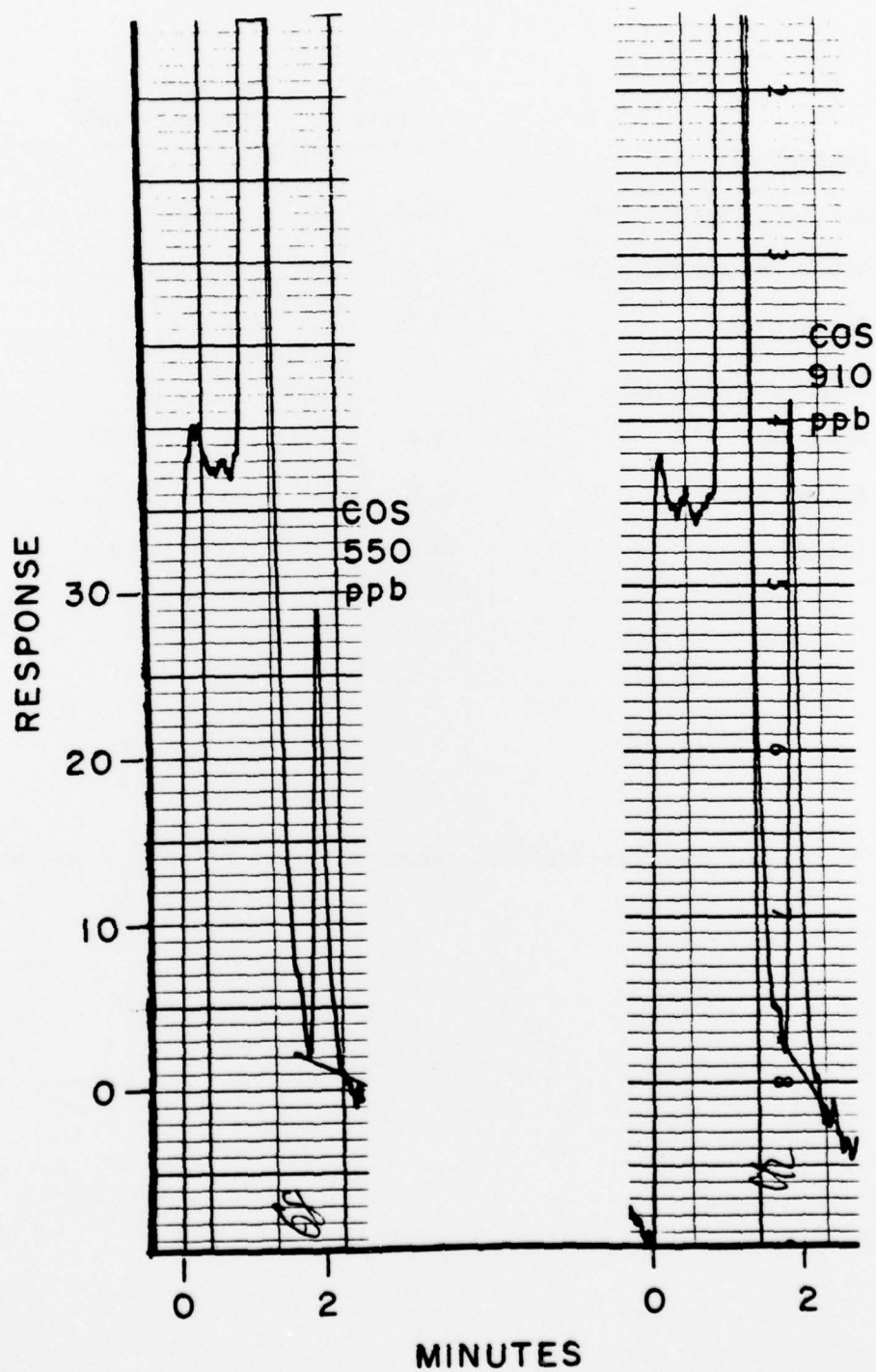


Table V

GC-MS Analyses of COS and CS<sub>2</sub>

	COS ppbv	Samples Studied	CS <sub>2</sub> ppbv	Samples Studied
<u>Ambient Air</u>				
A.E.R.E. Harwell, UK	0.56 ± .03	6	*	Several
O.G.C. Beaverton, USA	0.97 ± .12	3	.065	2
South Pole	0.78	1	.07	1
<u>Volcanic Emissions</u>				
Mauna Loa	48.6	1	46.4	2
Sulfur Bank	57.6	1	108.6	1
Iilewa	23.6	1	20.9	1

\* CS<sub>2</sub> was not detectable in direct analyses of ambient air at Harwell

## B. Concorde Air Sampling Program

### 1. Concorde Air Sampling System Design

The system as presently flown on the Concorde between Washington - London route was developed by the Department of Industry and the Department of the Environment, UK, as part of the United Kingdom's contribution to the Tripartite Agreement of 1976. A team comprising personnel from British Aerospace and Environmental and Medical Sciences Division, Harwell designed and built a self contained system suitable for flights on commercial Concorde flights. Important considerations that had to be considered when using experimental scientific apparatus in the cabin of a commercial flight were:

- a) No interference with comfort of passengers or crew, i.e. the pack should be stowed out of sight and should be inaudible.
- b) Apparatus must be packaged and cleared to airline equipment standards and approved by the Civil Aviation Authority. This involves use of approved equipment as well as emergency shut-down safety devices.
- c) The pack must not interfere with normal operation of the aircraft.
- d) Commercial penalties must be kept to a minimum. Performance penalties by virtue of the payload are much more severe in supersonic than in subsonic flight.

The package is designed to require no attention from the crew members during flight. The 5 functions it carries out are:

- a) Collect eight "grab samples" of air for subsequent laboratory analysis.
- b) Measure ozone continuously, apart from during the first 20 and last 15 minutes of the flight.
- c) Pass sample air through a filter membrane for particulate analysis or through an impregnated membrane for specific gas absorption

- d) Pass air through a cold trap for collection of a wide range of adsorbable gases.
- e) Record important parameters such as altitude, static temperature, ozone concentration and signals indicating the completion of specified events.

In more recent flights, the filter samples and the cold trap collections for adsorbable gases have been generally omitted from the sampling routine.

The system weighs 82 kg and is capable of installation in other aircraft (i.e. 28 volt d.c. and 115 volt 400 Hz a.c.). The entire package consists of two parts; a probe to bring air from outside the aircraft to the sampling pack and the pack itself that carries out the above functions. The probe assembly and sampling pack are installed unarmed before the outward flight from Heathrow to Dulles. During the ground servicing at Dulles the equipment is armed for operation. On arrival at Heathrow the sampling pack and probe are removed from the aircraft and returned to Harwell for analyses of the samples, data processing, inspection and refurbishing.

Since the apparatus had to pass airline equipment standards, all components had to be approved and an emergency shut-down safety device installed. The safety equipment included smoke and overheat sensors with follow-up shut-off controls. The four malfunction detectors used were:

- a) A smoke detector samples air from the center of the pack near the electronics and the electric motor.
- b) An overheat sensor is set at 100°C in the exhaust air duct.
- c) An overheat sensor is set at 70°C near the electronic control assembly.
- d) The electric motor contains an integral overheat switch set at 177°C.

All four detectors can initiate a mechanism which closes a shut-off valve in the cooling air supply and shuts off all electrical power.



The ozone monitor used is a Dasibi 1003AAS modified to operate on 115 volts 400 Hz a.c. The sample air from the probe is pressurized above ambient by two Metal Bellows MB158 pumps operated in series from a single 115 volt 400 Hz motor. Over a range of 3.4 to 7.5 psia at the intake pitot a pump outlet pressure of 30 to 45 psia are obtained. This provides sufficient over pressurization of the 215 ml bottles for several laboratory analyses. Since the climb, cruise and descent profiles flown between Washington and London vary very little, the system sequence for controlling the solenoid valves, switches and on-off and related automatic events is controlled by an Elremco cam-timer. The whole system functions automatically and no action from the crew is required. An Oxford Instrument's minilogger is used to record four channels of analogue data on C120 tape cassettes. Preflight calibration is carried out with preset test voltage corresponding to known values of ozone, temperature and altitude. The following data is recorded:

Channel 1 Timebase and event markers

Channel 2 Altitude

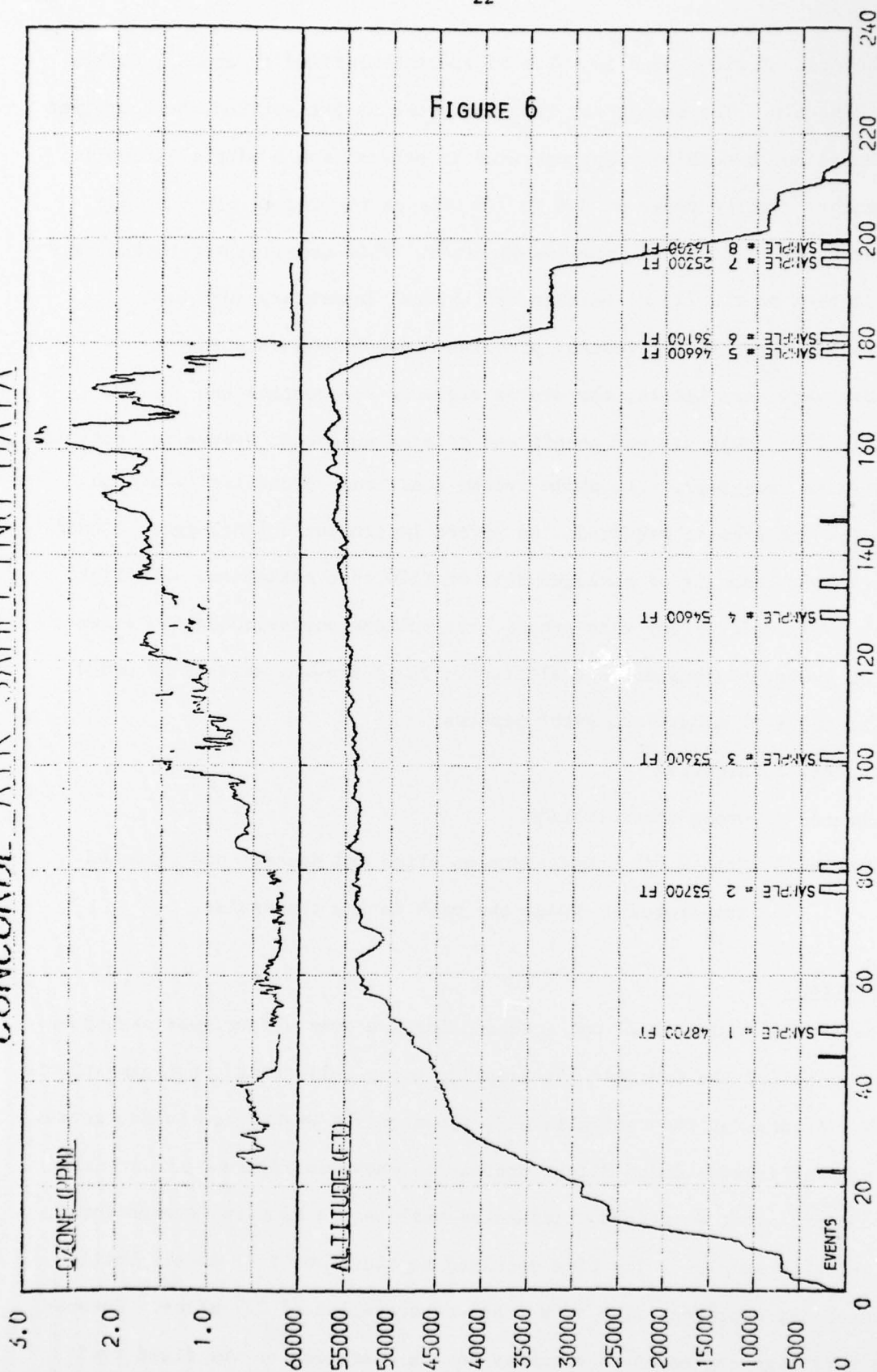
Channel 3 Ozone concentration

Channel 4 Static air temperature on climb and descent and selected temperatures inside the pack during the cruise.

## 2. Operation

Beginning in June 1977 and intended for use over a five year atmospheric monitoring period the Concorde Air Sampling began collecting upper atmospheric samples. At present the system is only flown on the Washington-London route. A typical Washington-London flight profile is shown in Figure 6 illustrating the ozone and altitude record obtained as well as the sampling events for the eight grab samples. The time required to flush and fill an air bottle is 72 seconds, representative of a distance travelled of ~27 miles. Because of the very high degree of consistency in the operation on the fixed route

## CONCORDE AIR SAMPLING DATA



FLIGHT SER. NO. 8. DATE 15 JAN 1978  
TYPICAL WASHINGTON - LONDON FLIGHT PROFILE

HARWELL



from Washington to London, the elapsed time down the track from take-off is adequate to set the timing for the sequenced events and indicate approximate sampling position. At lift-off, the activation of an under carriage weight switch causes the following functions:

- a) The mechanical timer begins to run.
- b) The data logger starts to record altitude, static air temperature, event marks and is in readiness for receiving ozone measurements.
- c) Ozone monitor receives electrical supply for its required 15 minute "warm-up".

During the climb and cruise, the timer initiates the following sequence of events.

- at 16 minutes, probe extends with main sampling system by-passed and probe connected directly vents overboard to purge contaminated air from the probe.
- at 18 minutes, system will shut down if probe is not fully extended.
- at 20 minutes, Metal Bellows twin pump starts up, ozone monitor inlet solenoid valve opens.
- at 50 minutes, airflow to the ozone monitor is inhibited while the first sample bottle is purged for 60 seconds and filled in 12 seconds. This is achieved by opening both solenoid valves on the sample bottle for the purge cycle and then closing the valve remote from the pump 12 seconds before the second solenoid valve.
- at 76, 100 and 126 minutes, the second, third and fourth bottles are filled in a similar manner.
- after 180 minutes, the bottle filling operation for the final four bottles is controlled by altitude signals, at 50,000; 40,000; 30,000 and 20,000 ft.

- at 190 minutes approximately, the pump and ozone monitor are stopped and the probe retracted. These operations are triggered by a signal 40 seconds after bottle No. 8 (20,000 ft) is filled.

The timer and data recorder are automatically switched off at touch-down.

### 3. Conclusion

Overall the Concorde Air Sampling Program is a very viable project. In fact it is unique in several aspects. It is the only regularly flown air sampling package on commercial aircraft. Especially noteworthy is that samples are obtained in both the lower stratosphere and upper troposphere. The NASA-GASP system using 747 aircraft in the U.S.A. has not been able to operate successfully its grab air sampler system nor can the 747's operate as far into the stratosphere or over as regularly scheduled flight path as flown by the Concorde between Washington and London.

The air samples obtained on the Concorde are of sufficient volume to enable multiple analyses of the same species or an extension of the measurements to different species. Accordingly it should be possible to exchange and/or store the samples collected until additional measurements are completed by collaborating laboratories. The over pressurization of the samples collected is an especially useful feature of the Concorde system.

The Concorde program has the advantages of a flexible air sampling project, an established record of operating reliable air sampling equipment, a reasonably routine sampling schedule, a flight profile that provides the needed representative mix of stratospheric and tropospheric samples, sufficient sample number (8) per flight to ascertain useful air chemistry data and state-of-the-art measurement capability at Harwell for the 7 species presently being studied.

In summary the design, operation and servicing requirements have proven reliable in the first year's operation and shake down flights. The system as

developed is suited to the capabilities of the Concorde flight profile between Washington and London. Significant data on ozone concentrations and the trace gases such as COS, CH<sub>3</sub>Cl, CH<sub>4</sub>, N<sub>2</sub>O are being obtained. The intended replacement of the valving system for the second year's operation should considerably improve the data obtained on other trace gases of interest. Recognition of the uniqueness, capabilities and potential for obtaining useful information on the chemical composition of the upper atmosphere with the Concorde program is apparent from the initial success of the program.

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